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Prepared by

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## Fourth Quarterly Progress Report

### ACCELERATED DETERIORATION OF ELASTOMERS

#### 1. Object

The object of this research is to find ways to degrade elastomers rapidly at or near room temperature. We are therefore studying the effects of soluble metal salts, hydrazines, and thiols on the rates of oxidation and chain scission of polyisoprene and polybutadiene in chlorobenzene as solvent.

#### 2. Summary

A number of complex cobalt compounds have been compared in oxidations of polyisoprene. To a first approximation, the cobaltous compounds are much alike, but the cobaltic compounds are less active or inactive (Section 4.2). An explanation for these results is proposed (Section 4.5). So far, metal compounds have served only to initiate chains by interacting with peroxides. A combination of t-butyl hydroperoxide and a cobaltous compound has given an immediate high rate of oxidation of undergraded rubber (Section 4.3). At high extents of oxidation, cobaltic compounds are precipitated. One such precipitate has been resolved into four distinct fractions, containing from 0.065 to 0.67 Co atom and from 2 to 3 atoms of oxygen per C<sub>5</sub> unit. All fractions contain enolate, alcohol, and complexed cobalt groups, but not many carboxyl groups (Section 4.1). Experiments on the effects of phenyl- $\beta$ -naphthylamine on cobalt-initiated oxidations have been undertaken. The balance of the opposing effects of these agents depends on their proportions, with the antioxidants (tentatively) producing more effect per unit weight (Section 4.4).

In the fast reaction between phenylhydrazine, polyisoprene, and oxygen, two molecules of oxygen are consumed per molecule of phenylhydrazine (Section 5.1). Preoxidation of the rubber does not have a large effect on this reaction (Section 5.2). A combination of phenylhydrazine and cobaltous acetylacetonate gives an effect intermediate between the fast but limited action of the hydrazine and the slower but long-sustained action of the metal (Section 5.3). Two other hydrazines show different behaviors without metals (Section 5.4). Experiments on the p-thiocresol-initiated oxidation of polyisoprene show that low concentrations of this reagent produce the quickest degradation, but that higher concentrations produce larger effects after considerable delay. We propose that some oxidation product of thiocresol may be the real and very active pro-oxidant (Section 5.5).



Our first tests on the oxidative degradation of polybutadiene indicate that it oxidizes one-half to one-tenth as fast as polyisoprene under comparable conditions, and that the net change in molecular weight is considerably less. Either the cleavage reaction of polybutadiene is less efficient, or it is offset by cross-linking (Section 5.6).

### 3. Preparation of Polyisoprene Solution

The original solution of undegraded polyisoprene used for most of the prior work was reported (Section 3.1 of Report No. 2) to contain 25.4 g of polymer/liter of chlorobenzene solution at 25°. The concentration has been redetermined by drying a thin film and found to be 2.30 wt %, corresponding to about 25.2 g of polymer/liter at 25°. This solution degraded over its period of use. Although the solution was stored in a brown bottle under nitrogen at room temperature, and although the viscosity of the original solution had not changed, its initial rate of degradation under oxygen, with or without added cobalt salts, was found to have increased substantially. Therefore, it has been discarded.

A new solution was prepared by dissolving some of the same lot of Shell cis-polyisoprene in benzene, filtering, and precipitating twice with methanol to remove antioxidants and other additives. The precipitate was dissolved in chlorobenzene and residual benzene and methanol were removed by distillation at about 50 mm pressure. Drying of a thin film gave the concentration as 2.10 wt %. The density of this solution was 1.096 g/ml at 25° and so it contained 23.0 g of polymer/liter of solution and was 0.338 M in isoprene units. The density of this solution was 1.077 g/ml at 50° and so actual concentrations at 50° are only 98.2% of those given in the tables and figures.

This rubber solution is very sensitive to light and air. If stored in amber bottles at room temperature, the initial viscosity does not change but its rate of reaction with oxygen increases. Storage in clear bottles leads to an obvious decrease in viscosity. We therefore store the solution in small, full, brown bottles under refrigeration. Once a bottle is partly used, it must be used within about a week or its contents discarded, even though the air space is filled with nitrogen.

### 4. Cobalt-Catalyzed Oxidations (K. Egger and Katherine Crawford Irwin)

#### 4.1. Investigation of Cobalt Precipitates

A solution of 26.3 g of oxidized polyisoprene per liter of chlorobenzene (oxidized polymer 4082, Section 3.1, Report No. 3) with 20 mmol/liter of cobaltous octanoate was agitated with oxygen under a reflux condenser for 10 days at 50°C. The rubber was thoroughly oxidized and degraded. The brown precipitate which formed was washed three times with warm benzene and dried; 320 mg of this solid was separated into four distinct fractions, all insoluble in chlorobenzene and other unpolar solvents, and with the properties listed in Table I. The elementary analyses gave scattered results on triplicate determinations. Difficulties

with C and H analyses are ascribed to inhomogenous samples; errors with oxygen and cobalt analyses may also arise from the uncertain compositions of the cobalt residues.

Most of the metal is in the trivalent oxidation state, with indications for divalent cobalt too. All the precipitates are amorphous (X-rays) and flame tests show no remarkable effect. The infrared studies in KBr on the initial precipitate and the fractions thereof show the following characteristics. Spectra of Fraction 1 and 3 show nearly identical IR absorption intensities and maxima. Since Fraction 1 contains only one-fifth as much cobalt as Fraction 3, none of the major absorption peaks is associated with cobalt. The spectra show large proportions of alcohol and free carbonyl groups (ketones and smaller amounts of aldehydes) and a very strong and relatively broad absorption at  $6.17 \mu$  attributed to a shifted, perturbed, carbonyl group. Fraction 2 has a relative higher alcohol content but is very low in free carbonyl. The perturbed carbonyl group is shifted even further up to  $6.28 \mu$ . The characteristic maximum in the  $6.2 \mu$  range attributed to a shifted carbonyl absorption. Such a shift would be expected for the antisymmetrical vibration of an ionized carbonyl group or for a keto-enol resonance system, such as in  $\beta$  diketones.

The extent of the carbonyl frequency shift in a keto-enol resonance system is a direct function of the double bond character of the C-C bond involved. The established shift from  $5.83 \mu$  for the free carbonyl to  $6.2$  for a perturbed keto-enol<sup>1</sup> resonance carbonyl suggests an almost full olefinic  $\alpha$ - $\beta$ -link in a  $\beta$  diketone. Cobalt would then form a metallic cholate with  $\beta$  diketones, emphasizing the olefinic character of the carbon link and shifting the carbonyl absorption to even higher wavelength.

None of the solids shows detectable free acid. For the following reasons the presence of ionized carboxyl groups in measurable or dominating amounts is excluded. The absorption at  $6.2 \mu$  does not change in intensity with variable amounts of cobalt in the compound. The water-soluble Fraction 2 undoubtedly contains trivalent cobalt. Unless they are specially stabilized by complexing, cobaltic salts are immediately decomposed by water to give cobaltous salts. The cobalt in Fraction 2 is in a stable trivalent complexed form. In none of the precipitations did detectable quantities of free acid groups show up. If ionized carboxyl groups account for the very strong band at  $6.2 \mu$ , some free carboxyl groups are expected, but none were detected in any fraction.

#### 4.2. Effects of Cobalt Complexes on Rates of Oxidation

Effects of a variety of cobalt complexes on the oxidation of polyisoprene were studied at  $50^{\circ}\text{C}$ . All these experiments were carried out with the chlorobenzene solution of oxidized polymer 4082, described in Section 3.2 of the Third Quarterly Progress Report. Pro-oxidant

<sup>1</sup>L. J. Bellamy, The Infrared Spectra of Complex Molecules, Wiley, N.Y., 1959, p. 142

Table I  
PROPERTIES OF PRECIPITATED COBALT FRACTIONS

	Whole Precipitate	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Solubility (All insoluble in $C_6H_6$ and $C_6H_5Cl$ )		Soluble AcMe Insoluble $H_2O$	Soluble $H_2O$ Insoluble AcMe	Insoluble AcMe and $H_2O$	Soluble AcMe and $H_2O$
Color	Pink-brown	Yellow	Pink	Brown	Brown
Weight	mg %	74.4 24.0	152.3 49.1	42 13.5	36.3 11.7
Elementary Analysis	C% H% Residue % Co% <sup>a</sup> O% <sup>b</sup>	58.42, 59.70, 58.65 7.39, 7.48, 7.44 4.25, 7.66, 5.12 3.76 30.15	30.5, 31.3, 31.96 4.59, 4.47, 4.50 28.38, 30.78, 28.65 21.03 42.51	39.48, 44.40, 45.22 5.16, 5.93, 5.90 31.80, 25.58, 24.86 18.23 30.65	Not Investigated
Approximate Em- pirical Formulas	$C_{16}.6H_{24}.8O_{10}.5Co$ $C_5H_7.5O_3.2Co.3$	$C_{76}.6H_{115}.9O_{29}.6Co$ $C_5H_7.6O_1.9Co.065$	$C_{7.5}H_{12.5}O_{7.5}Co$ $C_5H_8.4O_5Co.67$	$C_{12.2}H_{18.9}O_{5.2}Co$ $C_5H_7.8O_2.5Co.411$	

<sup>a</sup> Calculated on the basis that the residue is  $Co_3O_4$  (73.5%Co). Probably a mixed phase between  $Co_3O_4$  and  $Co_2O_3$  (71.1% Co) is actually weighed.

<sup>b</sup> By difference

<sup>c</sup> By direct oxygen analysis (Oita-Conway, Baumann). Since cobalt interferes with this determination and leads to relatively low results, the agreement between measured and calculated oxygen contents is reasonable.

effects on this polymer solution were measured for the following cobalt compounds:

$\text{Co}(\text{acac})_2$ . Cobaltous acetylacetonate is a  $\beta$ -diketone chelate with a tetrahedral structure and a magnetic moment,  $\mu$ , of 4.2.<sup>2</sup> The product used came from K and K Laboratories, Inc., Jamaica, New York (Lot 32614). This complex is soluble in acetylacetone and acetone, and sufficiently soluble in chlorobenzene.

$\text{Co}(\text{acac})_3$ . Cobaltic acetylacetonate is a nonelectrolytic inner complex with an octahedral structure.<sup>3,4</sup> It was prepared by adding dropwise an excess of  $\text{H}_2\text{O}_2$  to blue solution of  $\text{Co}(\text{acac})_2$  in acetylacetone. During this process the color changed to green. Evaporation of the solvent then gave green crystals which were recrystallized twice from 60% ethanol in water.  $\text{Co}(\text{acac})_3$  is sufficiently soluble in chlorobenzene for our purpose.

$\text{Co}(\text{py})_2\text{Cl}_2$ . Cobaltous pyridinium chloride is an ionic type complex with a violet color in solid state, resulting from a condensed octahedral structure with bridging chlorides between adjacent octahedra. In solution the complex is blue and has a tetrahedral structure with a  $\mu$  of 4.51.<sup>5</sup>  $\text{Co}(\text{py})_2\text{Cl}_2$  was prepared by melting  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in excess pyridine. After evaporation of the  $\text{H}_2\text{O}$  and pyridine the material balance indicated the expected composition.

$\text{Co}(\text{C}_5\text{H}_5)_2$ . Cobaltocene or dicyclopentadienylcobalt is commercially available through Arapahoe Chemicals Inc., Boulder, Colorado. It is a sandwich-type neutral compound with the cobalt atom located between the parallel planes of two cyclopentadiene rings. It is paramagnetic and soluble in hydrocarbons. Cobaltocene is a highly reactive compound which is readily oxidized by air, water, dilute acids, and  $\text{FeCl}_3$  to the extremely stable cobalticinium ion. A solution of 0.107 g cobaltocene/ml benzene was used.

$(\text{C}_5\text{H}_5)_2\text{Co}^+$ . Cobalticinium stearate (st) or octanoate (O) was prepared by heating commercially available cobalticinium acetate (Arapahoe Chemicals Inc.) with stearic or octanoic acid in stoichiometric amounts. After evaporation to dryness, solutions of the stearate and octanoate in chlorobenzene were prepared. The very stable cobalticinium ion has the same sandwich-type structure as cobaltocene. Its remarkable oxidation stability is shown by absence of reaction with ozone in glacial acetic acid, boiling concentrated sulfuric acid, and  $\text{H}_2\text{O}_2$ . Reduction of  $(\text{C}_5\text{H}_5)_2\text{Co}^+$  can be effected only by the action of complex hydrides

<sup>2</sup>A. E. Martell and M. Calvin, Chemistry of Metal Chelate Compounds, Prentice Hall, Inc., New York, 1952

<sup>3</sup>F. P. Dwyer, E. C. Gyarfas, Nature 168, 29 (1951)

<sup>4</sup>T. Moeller, E. Gulyas, J. Inorg. Nucl. Chem., 5, 245 (1958)

<sup>5</sup>R. S. Nyholm, Report to the Xth Solvay Council, Brussels, 1956

such as sodium borohydride or lithium aluminium hydride. Therefore, it cannot participate in an oxidation-reduction cycle.

$\text{CoSt}_2/\text{Co}(\text{C}_5\text{H}_5)_2\text{st}$ . A catalyst preparation by D. Van Sickle is probably a mixture of cobalticinium stearate and cobaltous stearate. Addition of concentrated hydrochloric acid to cobaltocene gave green crystals of  $[(\text{C}_5\text{H}_5)_2\text{Co}]_2(\text{CoCl}_4)$  on evaporation to dryness. This interesting compound contains both divalent anionic and very stable cationic trivalent cobalt. When dissolved in water, this compound probably decomposes into  $\text{Co}(\text{H}_2\text{O})_6^{++}$ ,  $2(\text{C}_5\text{H}_5)_2\text{Co}^+$ , and  $4\text{Cl}^-$ . This slightly purple precipitate was treated with sodium stearate and dried.

$\text{Co-O}$ . The cobaltous octanoate was the Nuodex product used in our earlier experiments (Table I, Report No. 2).

$\text{Co-st}$ . Cobaltous stearate was prepared by heating freshly precipitated and dried  $\text{CO}_2$ -free  $\text{Co}(\text{OH})_2$  in stearic acid.

The results from the measurements of the oxygen consumption with time are summarized in Fig. 1. Except for the cyclopentadienyl complexes, the various cobaltous compounds show similar behaviors and comparable efficiencies in their pro-oxidant effects. They produce the same steady initial rates for 10 to 15 hours, followed by a progressive decrease in rate.

$\text{Co}(\text{acac})_2$  and  $\text{Co}(\text{py})_2\text{Cl}_2$  seem superior to the other compounds in maintaining the initial rate. The steady rate with  $\text{Co}(\text{acac})_3$  is considerably slower than the initial rate with  $\text{Co}(\text{acac})_2$  but close to the ultimate steady rate with  $\text{Co}(\text{acac})_2$ . These results suggest that reaction of the more stable cobaltic form with peroxides is rate-determining in the cyclic catalytic process.

The extremely stable cobalticinium ion is apparently so stable that it does not react with peroxides. It not only has no pro-oxidant effect, it even retards oxidation. Neither does cobaltocene accelerate the rate of oxidation of the oxidized polymer 4082; oxygen and the oxidation products in the polymer solution oxidize cobaltocene too rapidly to the stable and inactive cobalticinium ion. The measured rates are therefore equal to those with cobalticinium ion. On the other hand, the precipitate consisting of cobaltous stearate and cobalticinium stearate behaves much like cobaltous stearate alone; any retarding effect of cobalticinium ion is not apparent.

The oxidation with  $\text{Co}(\text{py})_2\text{Cl}_2$  gave the usual color change and slowing of the rate of oxidation. We therefore attempted to stabilize the cobaltous form and maintain its activity by adding 10% of anhydrous pyridine to the chlorobenzene. Quite unexpectedly, the excess pyridine destroyed the catalytic activity of the complex. Further experiments then showed that 10% of pyridine in the solvent also acted as mild retarder for an ABN-initiated oxidation. These results are summarized in Fig. 2. The excess pyridine produces a different cobalt complex

with different redox properties (Section 4.5). In any event pyridine is an unpromising solvent for cobalt-initiated oxidations.

#### 4.3. Fast Oxidations of Undegraded Polyisoprene

Most of our previous experiments with metal compounds have employed solutions of degraded polymers of high oxygen contents. The object of the experiments in this Section, summarized in Fig. 3, was to determine what rates of oxidation could be attained with solutions of undegraded polyisoprene. Figure 3 shows that while t-butyl hydroperoxide has little or no ability to initiate oxidation chains at 50°, it markedly enhances the catalysis by cobalt, particularly in the early stages of the reaction. In the first three hours at 50°, about 0.08 mole of oxygen was absorbed per isoprene unit, a rate which should be of some practical interest.

#### 4.4. Effects of Antioxidants on the Accelerated Oxidation of Oxidized Polymer 4082

Since practical applications of accelerated degradations of elastomers will probably involve stocks containing antioxidants, some exploratory work was undertaken on solutions of one such combination. Oxidized polymer 4082 and the common rubber antioxidant, phenyl-β-naphthylamine (PBN) were employed. This chlorobenzene solution (Section 3.1 of Report No. 3) was 0.37 M in  $C_5H_8O_{2.1}$  units. Previous extensive oxidation of this solution favors the effects of cobalt in overcoming the effect of the PBN.

Experiments were first carried out with 1.3 to 1.9 millimolar ABN and various proportions of PBN to determine the relation between known rate of initiation, PBN concentration, and induction period. These results, summarized in Table II and Fig. 4, show that each molecule of PBN stops about 4 to 5 chains during the induction period. The oxidation then accelerates but the rate is lower than uninhibited rate. The number of chains stopped is appreciably greater than the 2.8 which has been found for diphenylamine.<sup>6</sup>

The experiments with cobaltous acetylacetonate show that this catalyst overcomes the effects of PBN faster than ABN at the same concentration, but that the induction period is still 29 hours with 8 moles of cobalt compound and 1400 moles of  $C_5H_8$  units per mole of PBN.

#### 4.5. Discussion

In chlorobenzene, the divalent cobalt compounds produce a fast initial rate of oxidation, attributed to an essentially noncyclic reaction of cobaltous compounds with rubber hydroperoxides or other reducible rubber oxidation products. Subsequently the rate of oxidation changes progressively to a slower steady rate, tentatively ascribed to the slower and cyclic redox reaction of the cobaltic species with

<sup>6</sup>J. R. Thomas and C. A. Tolman, J. Am. Chem. Soc., 84, 2930 (1962)

Table II

EFFECTS OF PHENYL- $\beta$ -NAPHTHYLAMINE ON THE RATE  
OF OXIDATION OF POLYISOPRENE AT 50°  
(All concentrations in millimoles/liter)

Expt. No. <sup>a</sup>	ABN <sup>b</sup>	PBN <sup>b</sup>	Co(acac) <sub>3</sub> <sup>c</sup>	IP <sup>c</sup> hours	R. <sup>d,e</sup> produced	Rate during IP hr <sup>-1</sup>	R./PBN
23	2.2	-	-	none	-	-	-
32	1.5	0.022	-	6	0.082 <sup>d</sup>	~6	~3.7
33	1.4	0.061	-	26.5	0.313 <sup>d</sup>	6.2	~5.1
19	1.6	0.07	-	22	0.302 <sup>d</sup>	5.6	~4.3
34	1.3	0.096	-	>80	-	5.6	"
20	1.9	0.27	-	>80	-	7.6	-
21	1.4	0.35	-	>80	-	7.6	-
22	1.7	0.64	-	>80	-	6.8	-
16	1.8	4.7	-	>120	-	5.2	-
27	-	-	2.3	none	-	-	-
26	-	0.03	2.2	none	0.135 <sup>e</sup>	-	-
25	-	0.26	2.0	28	1.17 <sup>e</sup>	6.1	-

<sup>a</sup>Lab. book 6708

<sup>b</sup>2,2'-Azobis-(2-methylpropionitrile), phenyl- $\beta$ -naphthylamine,  
and cobaltous acetylacetonate, respectively

<sup>c</sup>Induction period

<sup>d</sup>Free radicals produced during induction period, based on a  
first order rate constant for the decomposition of ABN at 50°  
of  $2.16 \times 10^{-6}$ /sec and 60% efficiency of radical production

<sup>e</sup>Calculated for 4.5 radicals produced per PBN consumed

rubber hydroperoxide. At the steady rate, cobaltous and cobaltic ions contribute equally to the cyclic initiation process, but the concentration of cobaltic ion is much higher because it is less reactive and rate-determining. At a high extent of oxidation, cobaltic complexes precipitate with products from the thoroughly oxidized polyisoprene.

So far we have found no indications of direct participation of cobalt catalysts in any propagation reaction. The pro-oxidant effect of cobalt compounds is a result of initiating new chains by decomposition of hydroperoxides. Except for chain cleavage associated with this peroxide decomposition, the relations between oxygen consumption (chain propagation) and chain cleavage seems to be independent of the initiator.

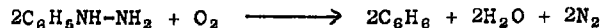
We neither expected nor found significant differences in the pro-oxidant effect of cobaltous compounds with distinctively different coordination species during the fast initial stage of oxidation. Here, peroxide concentrations seem more important. Among the more difficult, rate-determining reductions of cobaltic compounds with hydroperoxides, substantial distinctions appear. Thus the very stable, unreducible  $(C_5H_5)_2Co^+$  ion has no pro-oxidant effect, whereas  $Co(acac)_3$  has some catalytic effect.

Complexing effects of solvents may alter these relations. Although cobaltous salts are more effective (and less stable) than the cobaltic salts in chlorobenzene and nonpolar solvents, the opposite is true for glacial acetic acid.<sup>7</sup> In water only the divalent cobalt salts are stable and we could expect less catalytic effect. Excess pyridine stabilizes  $Co(py)_2Cl_2$  and nearly destroys its catalytic activity. The mechanisms of oxidation and reduction, i.e., the relations between different modes of electron transfer and ligand transfer, may also change with the reaction medium.

## 5. Degradations by Hydrazines and p-Thiocresol Jorge Heller and R. L. Walrath

### 5.1. Stoichiometry of Phenylhydrazine Oxidations

Chattaway<sup>8</sup> showed that phenylhydrazine and some of its derivatives are readily oxidized by air according to the relation:



In our studies of the degradation of rubber solutions by phenylhydrazine we have therefore assumed that one molecule of nitrogen is evolved for each molecule of hydrazine employed. This correction is incorporated in Fig. 5 but not in the remainder of Section 5. Figure 5 shows that 2.0 moles of oxygen are absorbed per mole of phenylhydrazine added to 50 ml of the 2.30 wt % solution of polyisoprene in chlorobenzene (after allowing for the indicated absorption of oxygen by the pure degassed solution in the absence of phenylhydrazine). For a useful relation between the hydrazine added and the number of cleavages, number average molecular weights have been requested. The highest oxygen absorption corresponds to one  $O_2$  per 77 isoprene units.

<sup>7</sup>M. H. Dean and G. Skirrow, Trans. Faraday Soc., 54, 849 (1958)

<sup>8</sup>F. D. Chattaway, J. Chem. Soc., 91, 1323 (1907)



### 5.2. Effect of Phenylhydrazine on Preoxidized Rubber

The following experiments show that preoxidation of a rubber solution has no more than a small effect on degradation by phenylhydrazine. Addition of 0.01 mmols of phenylhydrazine to 50 ml of rubber solution at 50° resulted in a decrease in flow time, over a few minutes, from 500 seconds to 65 seconds. When some of the original rubber solution was first shaken overnight with oxygen at 50°, the flow time dropped to 326 seconds. Addition of phenylhydrazine then caused a decrease in flow time to 37 seconds. Because we still have no good correlation of flow times with number-average molecular weights, these experiments cannot be interpreted quantitatively. Considering the high sensitivity of long flow times to degradation, there is no large effect of preoxidation.

### 5.3. Degradations by Combinations of Phenylhydrazine and Cobaltous Acetylacetonate

The fast but limited action of phenylhydrazine and the slower but sustained effect of cobaltous salts on the oxidative degradation of rubber solutions made desirable a test of a combination of these agents. The undegraded 2.10 wt % solution of polyisoprene in chlorobenzene and our most active cobaltous salt, the acetylacetonate, were used. Results are summarized in Fig. 6. As measured by either decrease in viscosity or absorption of oxygen, the combined effect of the two agents is intermediate between their individual effects. Since phenylhydrazine (or its decomposition products) eventually retard the catalytic action of cobaltous acetylacetonate, the abrupt cessation of the action of phenylhydrazine alone may be due to the formation of some retarder of oxidation as well as to exhaustion of phenylhydrazine. Aliphatic or unsubstituted hydrazines (Section 5.4) may not show these undesirable retarding effects of phenylhydrazine, and their combinations with cobalt salts may be more effective.

### 5.4. Substituted Hydrazines

Section 5.4 and Fig. 5 in Report No. 3 compared the effects of phenylhydrazine, hydrazine hydrate, and unsym.-dimethylhydrazine in degrading solutions of polyisoprene. Similar experiments have now shown that unsym.-diphenylhydrazine has no accelerating effect, and possibly a retarding effect, on degradation by oxygen. However, sym.-diphenylhydrazine (hydrazobenzene) has a slow but sustained effect close to that of unsym.-dimethylhydrazine. So far, only monosubstituted or unsubstituted hydrazines have exhibited very fast degrading actions. Further work on the effects of structures of hydrazines on rates of degradation and work on the mechanism of degradation are being deferred until the practical importance of such work for this contract has been determined.

### 5.5. Degradations by p-Thiocresol

Figure 7 summarizes the effects of various proportions of p-thiocresol on flow times (Section 3.3 of Report No. 2) and oxygen absorptions of 50-ml samples of our 2.30 wt % solution of polyisoprene in chlorobenzene. The results indicate either that thiocresol itself is not the sole oxidation catalyst or that it has a retarding effect as well as an accelerating effect. The highest initial rates of oxidation were obtained with the two lowest amounts of thiocresol used,  $0.5$  and  $1.0 \times 10^{-5}$  mole, the lowest rate with the highest amount tested,  $1.0 \times 10^{-4}$  mole. With an intermediate quantity,  $5.0 \times 10^{-5}$  mole, the highest rate of degradation was obtained, but only after an initial induction period. The highest quantity of p-thiocresol might give a similar acceleration after a longer induction period.

These results are of unusual interest. The experiment with  $10^{-5}$  mole of thiocresol absorbed 100 molecules of oxygen per mole of thiocresol in forty hours, proving a sustained catalytic effect. The high rate and induction period with  $5 \times 10^{-5}$  mole of thiocresol suggest that thiocresol itself has little effect but that it is converted to some other product which is the real and much more active catalyst. This conclusion has some parallel in the inhibiting properties of organic sulfides.<sup>8</sup> Another possibility is that chain initiation is sensitive to the hydroperoxide-thiol ratio.

Further experiments at lower concentrations and with longer times at high concentrations are in order. An oxidation product of thiocresol which is a more active oxidation catalyst is worth seeking. Some of the easily obtainable possibilities and t-butyl hydroperoxide-p-thiocresol combination will be examined.

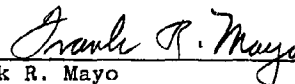
### 5.6. Cis-Polybutadiene

The polybutadiene solution which we used for our first degradation experiments with this polymer was found to contain suspended gel particles before oxidation. The suspension was therefore filtered to remove the gel; the rubber was precipitated with methanol and dried, and a new 5.00 wt % solution was made up in chlorobenzene. Fifty ml of this solution with  $10^{-5}$  moles of p-thiocresol took up oxygen about half as fast as the 2.3% solution of polyisoprene and the same amount of thiocresol (Fig. 7). For this absorption of oxygen the reduced relative flow time decreased to 0.26, a much smaller change than the decrease to less than 0.01 with polyisoprene. With  $10^{-5}$  moles of phenylhydrazine, the polybutadiene solution absorbed 1.5 ml of oxygen and the flow time was decreased from 145.9 seconds to 114.2 seconds in the same length of time, also a smaller change than with polyisoprene.

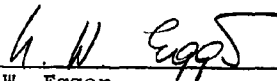
<sup>8</sup>D. Barnard, L. Bateman and J. I. Cunneen, Chapter 21 in Organic Sulfur Compounds, N. Kharasch, ed., Pergamon Press, 1961; D. Barnard, L. Bateman, E. R. Cole, and J. I. Cunneen, Chem. and Ind., 1958, 918

Because the above polybutadiene had been in solution for 4 months before the gel was removed, and because the expected gellation on oxidation was not observed, a new 10.7% by weight solution of Goodrich Ameripol CB, cis-polybutadiene, was made up, eliminating a relatively large amount of insoluble material. The density of this solution was 1.076 g/ml at 25° (1.057 at 50°), and so it was 2.13 M in C<sub>4</sub>H<sub>6</sub> units. Fifty ml of this solution was reacted with 10<sup>-4</sup> moles of ABN and oxygen overnight at 50°C. No gel was formed but the viscosity appeared to be reduced. Another portion of the solution was concentrated by distilling off chlorobenzene at reduced pressure to leave a 25.06% solution of rubber. This was reacted with oxygen and ABN in the same manner as in the preceding experiment without gellation.

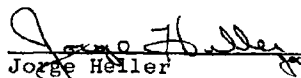
Our first results with the uncatalyzed oxidation of polybutadiene solution suggest that cis-polybutadiene absorbs oxygen only one-tenth as fast as cis-polyisoprene under comparable conditions and that there is considerably less net chain cleavage for the same degree of oxidation. We propose to check these conclusions carefully.



Frank R. Mayo  
Scientific Fellow



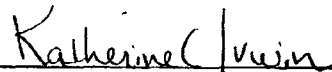
K. W. Egger  
Visiting Research Scientist



Jorge Heller  
Senior Polymer Chemist



Robert L. Walrath  
Organic Chemist



Katherine Crawford Irwin  
Chemist

FRM:KWE:JH:RLW:KCI:tf

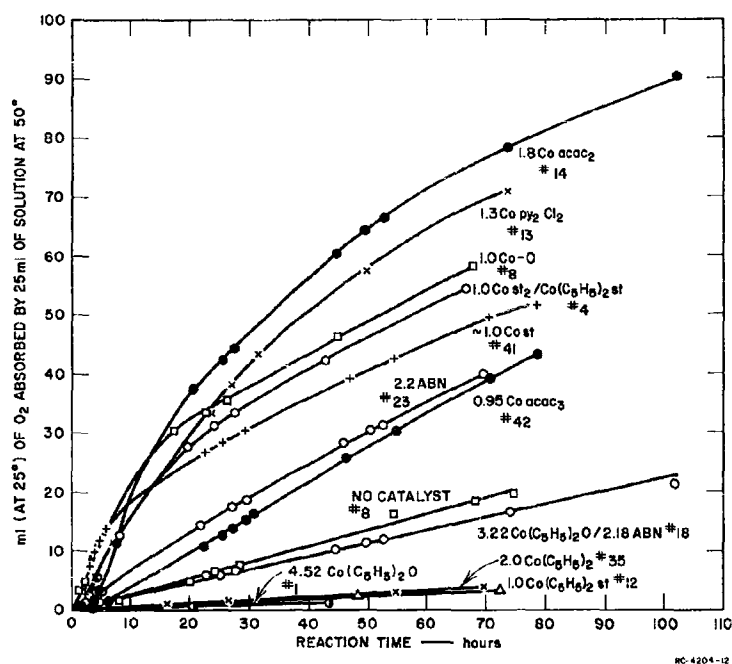


FIG. 1 RATES OF OXIDATION OF OXIDIZED POLYMER 4082 AT 50°C WITH DIFFERENT COBALT COMPOUNDS

Identifications indicate the cobalt component used, the concentration of the cobalt or ABN in millimoles/liter, and the experiment number in lab. book 6708

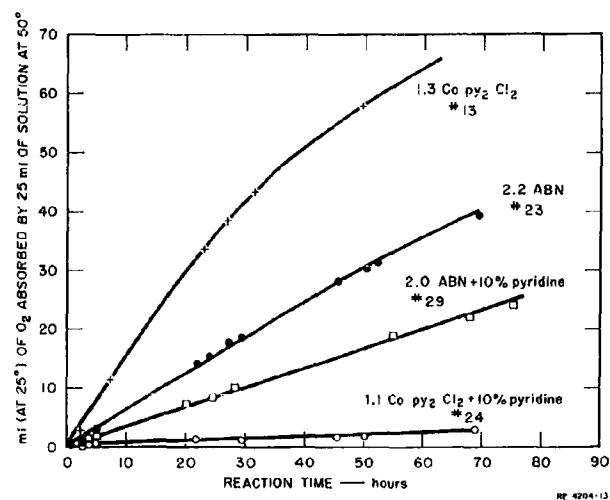


FIG. 2 EFFECT OF PYRIDINE WITH ABN AND  $\text{Co(py)}_2 \text{Cl}_2$  ON THE OXIDATION AT 50°C OF OXIDIZED POLYMER 4082. THE IDENTIFYING FIGURES INDICATE THE CONCENTRATION OF REAGENTS TESTED IN MILLIMOLES/LITER AND THE EXPERIMENT NUMBER IN LAB BOOK 6708

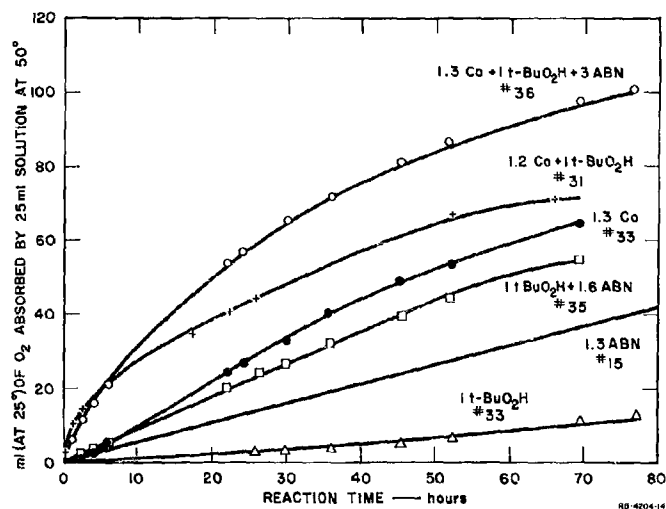


FIG. 3 THE EFFECT OF  $t$ -BUTYLHYDROPEROXIDE AND  $\text{Co}(\text{py})_2\text{Cl}_2$  ON THE RATE OF OXIDATION OF A SOLUTION OF 23.0 g UNDEGRADED CIS-POLYISOPRENE PER LITER CHLOROBENZENE AT  $50^\circ\text{C}$ . The identifying figures indicate the concentrations of added reagents in moles/liter and the number of the experiment in lab. book 6709. Expt. 15, with a similar solution, is taken from Table I in Report No. 2.

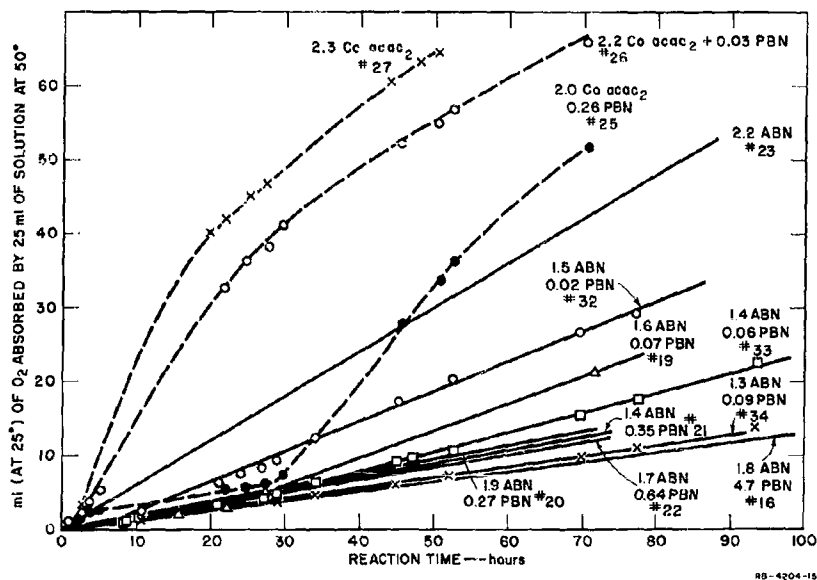
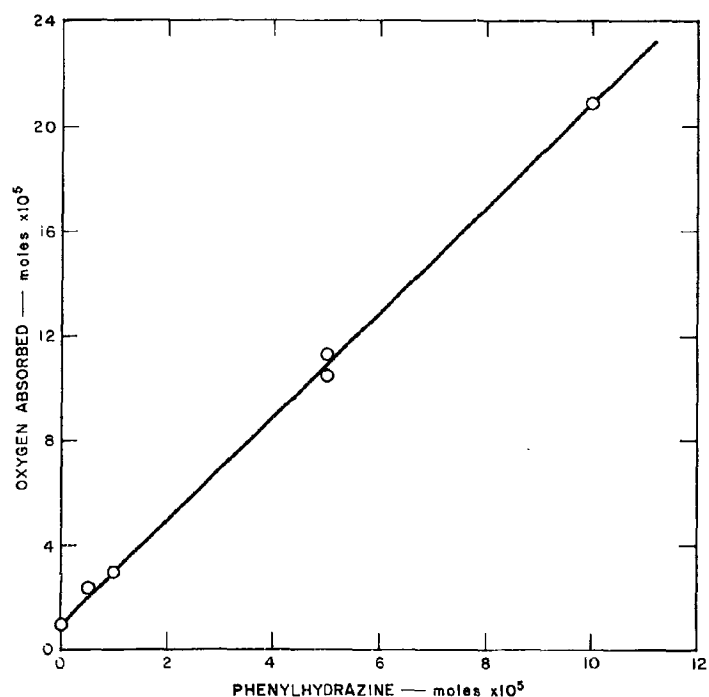
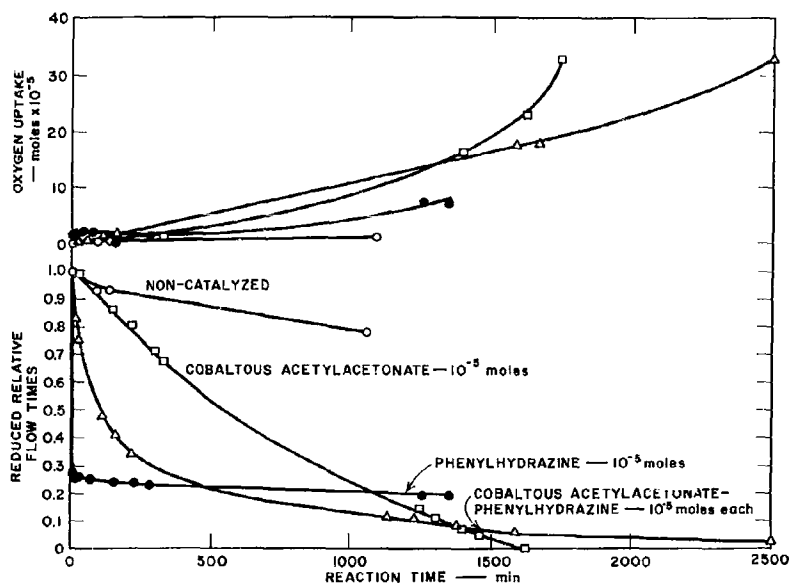


FIG. 4 EFFECT OF PHENYL-2-NAPHTHYLAMINE (PBN) ON THE RATE OF OXIDATION OF OXIDIZED POLYMER 4082 IN THE PRESENCE OF ABN OR COBALTOUS ACETYLACETONATE (acac) AT  $50^\circ\text{C}$ . Identifications in the figure indicate the concentrations of ABN and PNA in millimoles/liter and the number of the experiment in lab. book 6708.



RA-4204-16

FIG. 5 EFFECT OF PHENYLHYDRAZINE CONCENTRATION ON ABSORPTION OF OXYGEN AT 50°C BY 50 ml OF A 2.30% SOLUTION OF POLYISOPRENE IN CHLOROBENZENE



RB-4204-17

FIG. 6 EFFECTS OF PHENYLHYDRAZINE AND COBALTOUS ACETYLACETONATE ON THE DEGRADATION OF 50 ml SAMPLES OF 2.10 wt. % OF POLYISOPRENE IN CHLOROBENZENE

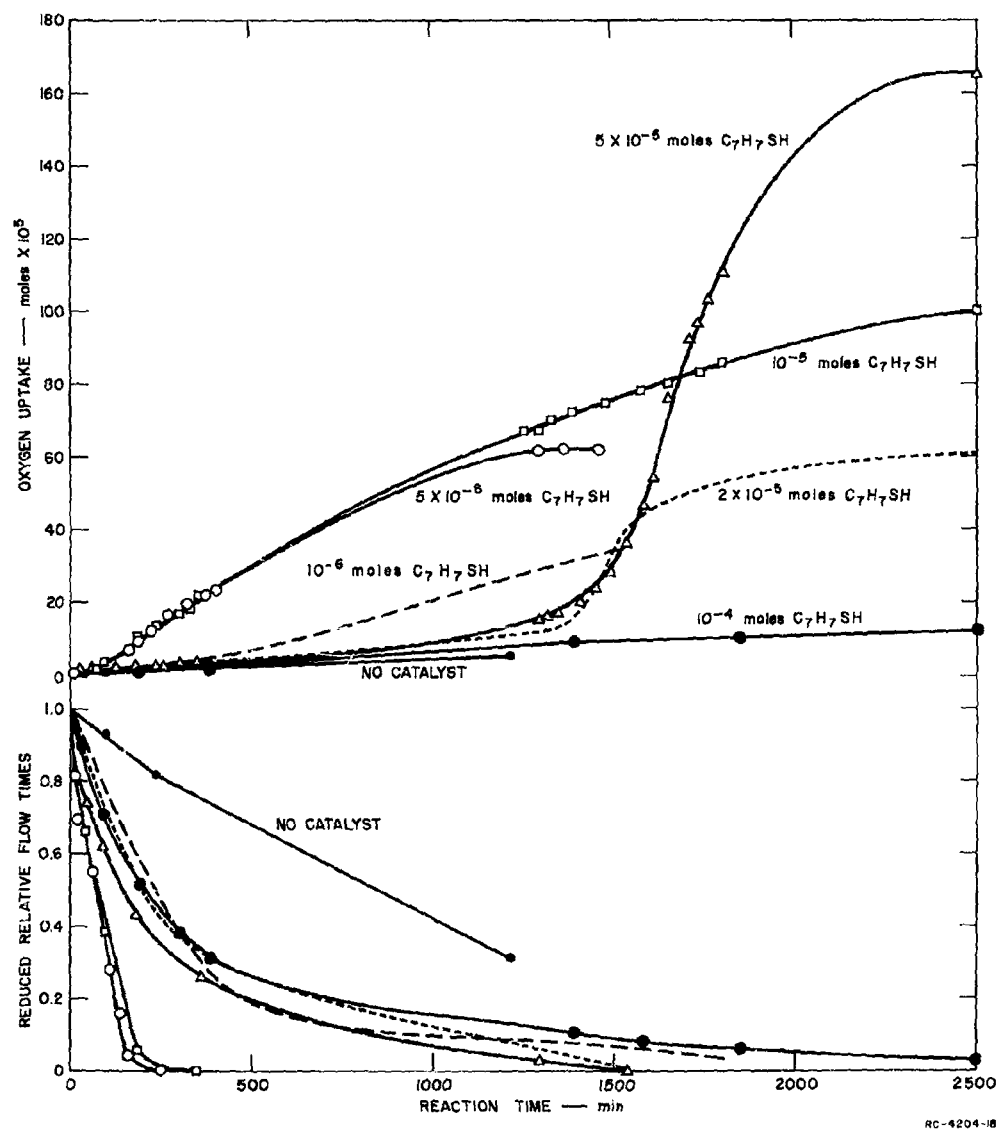


FIG. 7 EFFECT OF  $p$ -THIOCRESOL ON THE OXIDATIVE DEGRADATION AT  $50^\circ\text{C}$  OF 50 ml OF A 2.3 wt. % SOLUTION OF POLYISOPRENE IN CHLOROBENZENE

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